

# REPORT DOCUMENTATION PAGE

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13. ABSTRACT (Maximum 200 words)  The study of dissociation pathways, mechanism, and products for the energetic materials RDX [C <sub>3</sub> H <sub>6</sub> N <sub>3</sub> (NO <sub>2</sub> ) <sub>3</sub> ] and ADN [NH <sub>4</sub> N(NO <sub>2</sub> ) <sub>2</sub> ] in excited electronic valence and Rydberg states is undertaken. These spectroscopic and dissociation studies will be carried out on gas phase species that have been cooled and isolated in a supersonic expansion. A number of recent advances in experimental and theoretical techniques and capabilities have been incorporated into our laboratory so that these studies become feasible. The experiments are carried out on laser ablated materials that are cooled in a supersonic expansion and accessed with tunable photolysis lasers. Time-of-flight mass spectroscopy and fluorescence spectroscopy are employed to analyze the fragments. Covariance mapping of spectral data will aid in identifying the fragmentation pathways. Experiments will be supported by a theoretical effort of ab initio quantum chemistry calculations. These studies are important to the functioning of energetic materials in real applications because the ignition process can create excited electronic states of RDX and ADN and each state can have a different decomposition mechanism and set of products (e.g., CH <sub>2</sub> NNO <sub>2</sub> , CO <sub>2</sub> , NO, NO <sub>2</sub> , OH, etc.). System and material performance, as fuels and explosives, can be adjusted and tuned to maximize overall effectiveness and efficiency if RDX and ADN decomposition chemistry can be elucidated and understood as a function of electronic state.					
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FINAL REPORT (ORIGINAL AND TWO COPIES REQUIRED)

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TITLE OF PROPOSAL: Initial Steps in the Decomposition of Energetic  
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NAME OF INSTITUTION: Colorado State University  
AUTHOR OF REPORT: Elliot R. Bernstein

1. LIST OF MANUSCRIPTS submitted or published under ARO sponsorship during this reporting period, including JOURNAL REFERENCES:

PUBLISHED:

M. Foltin, G. J. Stueber, and E. R. Bernstein, "On the Growth Dynamics of Neutral Vanadium Oxide and Titanium Oxide Clusters," *J. Chem. Phys.* **111**, 9577 (1999) (copies included).

H.-S. Im and E. R. Bernstein, "On the Initial Steps in the Decomposition of Energetic Materials from Excited Electronic States," *J. Chem. Phys.* **113**, 7911 (2000) (copies included).

M. Foltin, G. J. Stueber, and E. R. Bernstein, "Investigation of the Structure, Stability, and Ionization Dynamics of Zirconium Oxide Clusters," *J. Chem. Phys.* **114**, 8971 (2001) (copies included).

SUBMITTED:

H.-S. Im and E. R. Bernstein, "Photodissociation of NO<sub>2</sub> in the Region of 217 to 237 nm: Nascent NO Energy Distribution and Mechanism," *J. Phys. Chem A*, accepted.

2. SCIENTIFIC PERSONNEL supported by this project and HONORS/AWARDS/DEGREES received during this reporting period:

Supported Personnel: Hoong-Sun Im (postdoc)  
Martin Foltin (postdoc)  
Jianlong Yao (postdoc)  
Guido Stueber (postdoc)

Elliot R. Bernstein (PI) was appointed to the Editorial Boards of *J. Am. Chem. Soc.* and *J. Chem. Phys.* Also was a symposium organizer at the Pacifichem 2000 meeting.

3. Report of INVENTIONS (BY TITLE ONLY):

N/A

#### 4. SCIENTIFIC PROGRESS AND ACCOMPLISHMENTS – Describe research progress and accomplishments, including significant theoretical or experimental advances.

We include a review of our metal oxide studies in this report because the techniques we developed for this work have enabled us to access RDX, HMX, and other highly energetic materials. This development has not previously been available to energetic materials research and has thus been an important and time-consuming part of our progress in this area.

Cluster growth dynamics of vanadium oxide and titanium oxide clusters produced by laser ablation of vanadium and titanium metal in a He gas flow seeded with up to 2% O<sub>2</sub> are studied by covariance mapping time-of-flight mass spectrometry. Covariance mapping enables the recognition of two different distribution components in the overall homogeneous mass spectra for both vanadium oxide and titanium oxide cluster systems. The oxygen rich component Or shows small correlated fluctuations while the oxygen poor component Op shows large correlated fluctuations. These two cluster distribution components are observed at low ablation laser powers and low expansion gas concentrations. Fluctuations of small vanadium oxide clusters (V<sub>2</sub>O, V<sub>2</sub>O<sub>2</sub> and V<sub>2</sub>O<sub>3</sub>) and small titanium oxide clusters (Ti<sub>2</sub>O<sub>2</sub> and Ti<sub>2</sub>O<sub>3</sub>) are covariance determining. The less fluctuating V<sub>2</sub>O<sub>3</sub> and Ti<sub>2</sub>O<sub>3</sub> clusters are "nuclei" for the oxygen rich components Or. The more fluctuating V<sub>2</sub>O and Ti<sub>2</sub>O<sub>2</sub> are "nuclei" for the oxygen poor components Op. Correlated fluctuations or covariances within each distribution component are constant. Covariances for the different distribution components are different. Studies of mass spectra and covariances as functions of ablation laser power and expansion gas concentration imply that V<sub>2</sub>O and Ti<sub>2</sub>O<sub>2</sub> clusters are formed in different regions of the ablation plasma plume than V<sub>2</sub>O<sub>3</sub> and Ti<sub>2</sub>O<sub>3</sub>. We suggest that V<sub>2</sub>O<sub>3</sub> and Ti<sub>2</sub>O<sub>3</sub> are formed in the hot and optically dense region near the ablated metal surface and that V<sub>2</sub>O and Ti<sub>2</sub>O<sub>2</sub> are formed in the colder plasma region farther away from the ablated metal surface. Larger vanadium oxide and titanium oxide clusters grow from these small clusters by very specific pathways which involve only uptake of VO or VO<sub>2</sub> and TiO<sub>2</sub>, respectively.

Photodissociation of NO<sub>2</sub> in the region of 217-237 nm is investigated by probing the nascent NO generated using a one-laser photofragmentation/fragment-detection technique. By mixing O<sub>2</sub> in the sample (20% to 100%) and by setting proper detection timing, only mass resolved excitation spectra (MRES) of photofragmented NO are obtained and examined. The nascent NO spectrum changes depending on the intensity (W/cm<sup>2</sup>) of the laser beam. For low laser intensity, the dissociation of NO<sub>2</sub> produces rotationally and vibrationally cold NO through the NO<sub>2</sub> 2 <sup>2</sup>B<sub>2</sub> ( $\tilde{B}$ ) excited state. Excess energy for this photofragmentation is ~0.4 eV at 226 nm. This excess energy is distributed almost entirely to the kinetic energy of NO(X <sup>2</sup>A<sub>2</sub>) and O(<sup>1</sup>D) products. The spectrum of photofragmented NO becomes very crowded as the laser intensity is increased because higher rotational and vibrational levels of NO become populated through multiphoton excitation and eventual photofragmentation of NO<sub>2</sub> from higher energy electronic states. The rotational temperature of NO is ca. 200 K for high laser intensity, and less than 30 K for low laser intensity. Near 230 nm, a rovibronic spectrum is observed that cannot be attributed to NO even though it is detected in the NO mass channel. The time-of-flight mass spectrum linewidth for photofragmented NO in this photolysis region increases by a factor of two to about 40 ns (estimated NO kinetic energy is 0.40 ± 0.04 eV) for high laser intensity. These observations lead to the conclusion that a higher electronic state of NO<sub>2</sub> has been accessed to generate highly

excited NO through multiphoton absorption processes for the high laser intensity experiments. Such intermediate states can be Rydberg, ion pair, or other high energy states of  $\text{NO}_2$  accessed by multiphoton absorption.

Decomposition studies of hexahydro-1,3,5-trinitro-1,3,5-triazine ( $\text{RDX-C}_3\text{H}_6\text{N}_6\text{O}_6$ , see Figure 1) isolated in the gas phase and cooled in a supersonic expansion are reported for the excited electronic state near 225 nm. The RDX is handled safely and effectively through matrix-assisted laser desorption (MALD) of a thin film of RDX/R6G laser dye (1:1) adsorbed on an aluminum oxide coating on an aluminum drum. The aluminum oxide coating is generated by plasma electrolytic oxidation of aluminum. The contribution of MALD and supersonic molecular beam techniques generates intact and cold RDX molecules isolated in the gas phase. Two basic conclusions are reached in this study: 1. photodissociation of RDX at ca. 225 nm generates NO as an initial product; and 2. nascent NO thus generated is vibrationally hot ( $T_{\text{vib}} \sim 1800$  K) and rotationally cold ( $T_{\text{rot}} \sim 20$  K).

The growth dynamics, stabilities, and structures of small zirconium oxide clusters ( $\text{Zr}_n\text{O}_m$ ) are studied by covariance mapping time-of-flight mass spectrometry and density functional theory calculations. The zirconium oxide clusters are produced by laser ablation of zirconium metal into a helium gas flow seeded with up to 7%  $\text{O}_2$ . The neutral ( $\text{Zr}_n\text{O}_m$ ) cluster distribution is examined at high and low ionization laser intensities. At high ionization laser intensities ( $\sim 10^7$  W/cm<sup>2</sup>) the observed mass spectra consist entirely of fragmented, nonstoichiometric clusters of the type  $[(\text{ZrO}_2)_{n-1}\text{ZrO}]^+$ , while in case of lower laser intensities ( $\sim 0.2 \times 10^7$  W/cm<sup>2</sup>), cluster fragmentation is strongly reduced and predominantly stoichiometric clusters  $(\text{ZrO}_2)_n^+$  appear. Under such gentle conditions,  $(\text{ZrO}_2)_5^+$  is found to be much more abundant than its neighboring clusters  $(\text{ZrO}_2)_n^+$ ,  $n = 1, 2, 4, 6, 7, 8$ . The unusually high signal intensity of the  $\text{Zr}_5\text{O}_{10}^+$  ion is found to be due to the high stability of the  $(\text{ZrO}_2)_5$  neutral cluster. Density functional theory calculations show a number of different conceivable isomer structures for this cluster and reveal the most likely growth pattern that involves the sequential uptake of  $\text{ZrO}_2$  units by a  $(\text{ZrO}_2)_4$  cluster to yield  $(\text{ZrO}_2)_5$  and  $(\text{ZrO}_2)_6$ . Based on a series of different density functional theory and Hartree-Fock theory calculations, and on kinetic modeling of the experimental results, isomer structures, growth mechanisms, and stability patterns for the neutral cluster distribution can be suggested. The  $(\text{ZrO}_2)_5$  structure most stable at temperatures less than 3000 K is essentially a tetragonal pyramid with five zirconium atoms at the vertices, whereas an octahedral structure is the main building block of  $(\text{ZrO}_2)_6$ . Modeling of the covariance matrix over a wide range of ionization laser intensities suggests that  $(\text{ZrO}_2)_n$  neutral clusters absorb two photons of 193 nm radiation to ionize and then, for high laser intensity, the ion absorbs more photons to fragment.

In addition, we have studied N-nitropyrrolidine ( $\text{C}_4\text{H}_8\text{N}_2\text{O}_2$ ) and N-nitropiperazine ( $\text{C}_5\text{H}_{10}\text{N}_2\text{O}_2$ ) as model compounds for energetic nitramines. Both give, in the decomposition as done for RDX, the product nitrosamine ( $\text{C}_4\text{H}_8\text{N}_2\text{O}$  and  $\text{C}_5\text{H}_{10}\text{N}_2\text{O}$ ). This is very interesting mechanistically, as we suggest that the first step for RDX dissociation is thereby loss of oxygen from a nitrosamine group and the release of NO as found in our work above. The difference between RDX, HMX, etc., and the model compounds is thus the stability of the nitrosamine species. These are very new and very important findings for energetic nitramine systems.

5. TECHNOLOGY TRANSFER – Describe any specific interactions or developments which would constitute technology transfer of the research results. Examples include patents, initiation of a start-up company based on research results,

interactions with industry/Army R&D Laboratories or transfer of information which might impact the development of products.

N/A